INTERNATIONAL STANDARD

ISO 15038

First edition
1999-06-01

Plastics — Organic-perester crosslinking agents for unsaturated-polyester thermosetting materials — Determination of active-oxygen content

Plastiques — Agents de réticulation à base de peresters organiques pour matériaux thermodurcissables à base de polyesters non saturés — Détermination de la teneur en oxygène actif

Reference number
ISO 15038:1999(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 15038 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

Annex A forms a normative part of this International Standard.

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet iso@iso.ch

Printed in Switzerland

Plastics — Organic-perester crosslinking agents for unsaturated-polyester thermosetting materials — Determination of active-oxygen content

WARNING — This International Standard involves the handling of dangerous products such as peroxides. The wearing of safety glasses is therefore essential throughout the test.

1 Scope

This International Standard specifies a method of determining the total active-oxygen content of organic peresters.

It applies to those peresters used to initiate crosslinking of unsaturated-polyester thermosets.

The peresters most widely used in the crosslinking of unsaturated-polyester resins are given in Table 1.

Table 1 — Main types of organic perester

Perester	Molecular mass
tert-Butyl perbenzoate	194,2
tert-Butyl 2-ethylperhexanoate	216,3
iso-Propyl *tert*-butylperoxy carbonate	176,2
tert-Amyl 2-ethylperhexanoate	230,3
tert-Amyl perbenzoate	208,3
tert-Butyl 3,5,5-trimethylperhexanoate	230,4

Butyl peresters may contain traces of *tert*-butyl hydroperoxide (TBHP), the active oxygen in which can be determined separately from that in the perester itself (see annex A). The active-oxygen content of the perester alone can then be obtained by subtraction.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

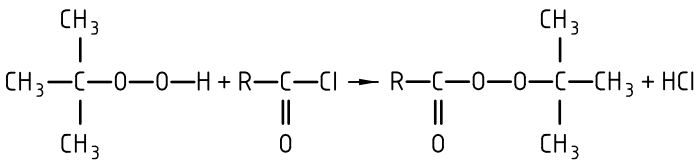
ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

3 Terms and definitions

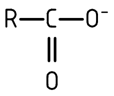
For the purposes of this International Standard, the following definitions apply:

3.1
active oxygen of an organic perester
oxygen, liberated by an organic perester, capable of initiating crosslinking of organic compounds which have a C=C double bond such as unsaturated-polyester resins

3.2
perester
a peroxide obtained by the reaction of an acid chloride with a hydroperoxide in accordance with the following equation [using *tert*-butyl hydroperoxide (TBHP) as an example]:

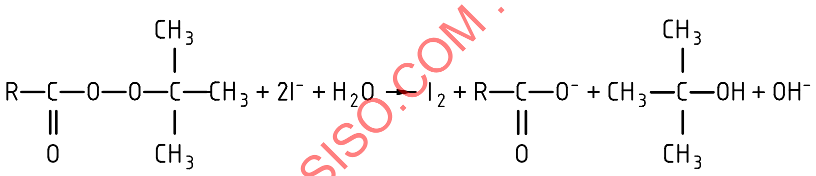


NOTE The compound obtained has the properties of a peroxide group – O – O – and those of an organic-acid group



4 Principle

A test portion of the perester is reacted with potassium iodide in a propanol/acetic acid medium in the presence of copper(II) chloride. The iodine released is then determined quantitatively using a standardized sodium thiosulfate solution.



$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

5 Reagents

5.1 Water, grade 3 as defined in ISO 3936, for use in preparing all the solutions listed below and in all other operations.

5.2 Sodium thiosulfate, standardized solution, $c(Na_2S_2O_3)$ = 0,1 mol/l.

5.3 Glacial acetic acid.

5.4 Isopropanol, analytical grade.

5.5 Copper(II) chloride, 10 g/l aqueous solution (shelf life 6 months).

5.6 Potassium iodide, saturated solution freshly prepared from 100 g of KI and 100 ml of water (shelf life 1 day).

5.7 Nitrogen or **carbon dioxide**, purity ⩾ 99,9 %.

6 Apparatus

6.1 Conical flask, capacity 200 ml, with a 29/32 ground-glass neck and stopper.

6.2 Analytical balance, accurate to 0,1 mg.

6.3 Weighing tube, glass dish or **tared syringe**.

6.4 One-mark pipettes, capacity 1 ml and 5 ml, as specified in ISO 648.

6.5 Burette, capacity 50 ml, as specified in ISO 385-1.

6.6 Graduated test tubes, capacity 50 ml and 20 ml.

6.7 Magnetic stirrer.

7 Procedure

Pour 40 ml of isopropanol (5.4) and 15 ml of acetic acid (5.3) into the conical flask (6.1).

Pass a gentle flow (approximately 150 ml/min) of nitrogen or carbon dioxide (5.7) through the flask above the surface of the liquid. Maintain this gas flow until the conical flask is stoppered (see below).

Using a pipette (6.4), add exactly 1 ml of copper chloride solution (5.5).

Stir gently on the magnetic stirrer (6.7) to homogenize.

Using a weighing tube, dish or tared syringe (6.3), weigh, to the nearest 0,1 mg, approximately 2 mmol of the perester to be analysed.

Place the test portion in the conical flask, stopper the flask and stir until the test portion is dissolved.

Using a pipette (6.4), add 4 ml of potassium iodide solution (5.6). Re-stopper the conical flask and stir again.

Allow to stand away from light for 30 min at ambient temperature (for certain peresters, this length of time is not necessary, and a shorter time may be used provided it can be demonstrated that the results are not affected).

Add 50 ml of water (5.1) and titrate with sodium thiosulfate solution (5.2) until the solution becomes completely colourless.

Carry out a blank determination under the same conditions but omitting the test portion.

Repeat the procedure on a second test portion.

8 Expression of results

8.1 Total active-oxygen content

The total active-oxygen content $(\mathrm{AO})_\mathrm{T}$, in mass %, is calculated using the equation

$$(\mathrm{AO})_\mathrm{T} = \frac{(V_1 - V_2) \times c \times 0{,}8}{m}$$

where

V_1 is the volume, in millilitres, of sodium thiosulfate solution (5.2) used to titrate the test portion;

V_2 is the volume, in millilitres, of the sodium thiosulfate solution used to titrate the blank;

c is the concentration, in moles/litre, of the sodium thiosulfate solution;

m is the mass, in grams, of the test portion.

8.2 Perester content

In the absence of any traces of *tert*-butyl hydroperoxide (TBHP), the perester content, in mass %, of the sample is calculated from the active-oxygen content $(\mathrm{AO})_\mathrm{T}$ by simple proportion, using the molecular mass of the perester concerned.

$$\text{Perester content} = \frac{(\mathrm{AO})_\mathrm{T} \times M}{16}$$

where M is the molecular mass of the perester.

In the case of a diperester, the ratio $M/16$ is replaced by $M/32$.

8.3 Correction for TBHP

If there are traces of TBHP, the active-oxygen content of the TBHP alone, $(\mathrm{AO})_\mathrm{TBHP}$, can be determined by the method given in annex A.

The active-oxygen content of the perester alone, $(\mathrm{AO})_\mathrm{PER}$, is obtained by subtraction:

$$(\mathrm{AO})_\mathrm{PER} = (\mathrm{AO})_\mathrm{T} - (\mathrm{AO})_\mathrm{TBHP}$$

The perester content of the sample is then calculated as in 8.2, using $(\mathrm{AO})_\mathrm{PER}$ instead of $(\mathrm{AO})_\mathrm{T}$.

9 Precision

Following a round-robin test organized in France involving four laboratories, each of which carried out five determinations on the same perester sample, the precision of this method has been determined to be as follows:

For an active-oxygen content of 10 %, s_r = 0,017, r = 0,05, s_R = 0,035 and R = 0,1

where

s_r is the within-laboratory standard deviation;

s_R is the between-laboratory standard deviation;

r is the repeatability, i.e. the value below which the difference between two results, each the mean of duplicates, obtained on identical material by the same operator in the same laboratory within a short interval of time using the standardized test method would be expected to lie;

R is the reproducibility, i.e. the value below which the difference between two results, each the mean of duplicates, obtained on identical material by operators in different laboratories within a short interval of time using the standardized test method would be expected to lie.

10 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all details necessary for complete identification of the material tested (type, origin, trade designation, etc.);

c) the individual results and their average;

d) the date of the determination;

e) details of any operation not mentioned in this International Standard, as well as details of any incident likely to have had an effect on the results.

Annex A
(normative)

Active-oxygen content of *tert*-butyl hydroperoxide

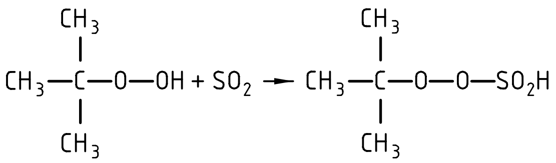
A.1 Scope

This annex specifies a method for the determination of the active-oxygen content of *tert*-butyl hydroperoxide (TBHP) in a *tert*-butyl perester.

The method is not aplicable if the product also contains other hydroperoxides, peracids or ketone peroxides.

A.2 Principle

The TBHP is reduced in a toluene-methanol medium using SO_2 dissolved in a pyridine-methanol mixture. The excess SO_2 is titrated with iodine solution.



$$H_2SO_3 + H_2O + I_2 \rightarrow SO_4^{2-} + 2I^- + 4H^+$$

A.3 Reagents

A.3.1 Water, grade 3 as defined in ISO 3696, for use in preparing all the solutions listed below and in all other operations.

A.3.2 Toluene, analytical grade.

A.3.3 Iodine, aqueous solution, $c(I_2) \approx 0{,}05$ mol/l (shelf life 1 month).

Dissolve approximately 12,7 g of iodine in 40 g of 500 g/l potassium iodide solution and make up to 1000 ml with water (A.3.1).

A.3.4 Methanol, analytical grade.

A.3.5 Pyridine, analytical grade.

WARNING — Pyridine is toxic. Avoid inhalation of vapour. Prevent contact with skin and eyes. Work under a fume hood or in a well ventilated area.

A.3.6 Sulfur dioxide (SO_2), 0,05 mol/l solution in a 10:1 methanol-pyridine mixture (shelf life 2 weeks).

There are two possible ways of preparing this solution: